Inorg. Chem. **2003**, *42*, 4522–4524

Inorganic Chemistry
Communication

Crystals from Concentrated Glyme Mixtures. The Single-Crystal Structure of $LiClO_4$

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Received May 15, 2003

A procedure for the preparation of high-quality single crystals from concentrated glyme mixtures is presented. Anhydrous single crystals of $LiNO_3$ and $LiClO_4$ were prepared in this manner, and the single-crystal structure of $LiClO_4$ (orthorhombic, *Pnma*, $a = 8.6447(12)$ Å, $b = 6.8512(10)$ Å, $c = 4.8254(7)$ Å, $Z = 4$) was determined as an example. This procedure is expected to be widely applicable for not only salts but also a wide range of other materials solvated by glymes.

In general, it is difficult to grow high-quality anhydrous single crystals of many salts. Slow solvent evaporation typically leads to the formation of crystalline solvates instead of pure salt. Removal of the solvent results in powders rather than salt single crystals. Salts containing smaller, harder cations such as Li^+ are the most problematic. Many crystal structures of relatively simple salts remain unknown for this reason. Powder diffraction techniques may be employed as an alternative to single-crystal determination, and, recently, the crystal structures of $LiCF_3SO_3$ and $LiN(SO_2CF_3)_2$ have been determined from powder data.[1] Despite advances in powder diffraction structural determination techniques, however, these remain difficult. In addition, single-crystal data invariably results in more precise structural solutions than powder data.[2] Single-crystal structural characterization thus remains the technique of choice when available.[3]

A novel technique for preparing large, high-quality single crystals of salts is presented here utilizing highly concentrated glyme−salt mixtures. Glymes consist of ethylene oxide oligomers, $CH_3O-(CH_2CH_2O)_x-CH_3$, where G1−G4 correspond to $x = 1-4$, respectively. As such, they are very effective at coordinating cations due to the strong donor character of the ether oxygen electron lone pairs and to the flexibility of the ethylene oxide chains. A rich variety of glyme−salt amorphous and crystalline solvates form. Highly concentrated liquid glyme−salt mixtures may be prepared, however, which are thermodynamically unstable. The crystallization technique described here takes advantage of this.

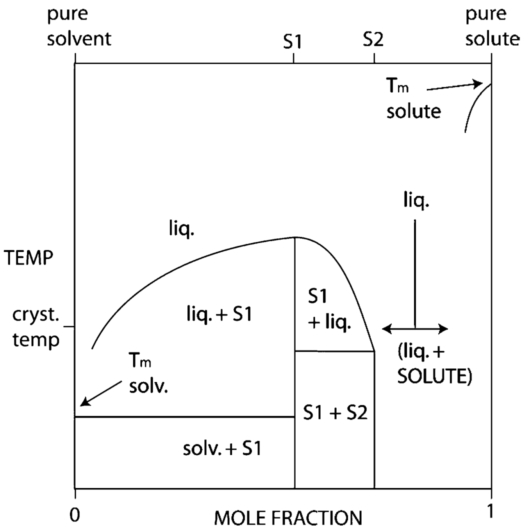

Figure 1. Generic phase diagram illustrating solute single-crystal preparation technique.

Figure 1 illustrates the technique with a generic phase diagram. In this example, two crystalline solvate phases, S1 and S2, form in the solvent−solute mixtures. The more concentrated S2 solvate, however, is amorphous at the crystallization temperature. The solute is dissolved in the solvent to a concentration greater than that of S2. Such highly concentrated mixtures may be prepared with glymes and salts since numerous amorphous ion aggregate solvate structures are possible with the multidentate, flexible ligands. The nonequilibrium aggregates formed slowly phase separate into single crystals of the solute and a liquid glyme−solute phase with a concentration close to that of the S2 solvate.

For example, high-quality block single crystals of $LiNO_3$ grew in concentrated liquid tetraglyme $(G4)_n-LiNO_3$ mix-

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10.1021/ic034518q CCC: $25.00

tures ($n = 0.5$ and 0.4) over several weeks.[4] The identity of the crystals was verified using single-crystal X-ray diffraction. Less concentrated ($n \geq 0.6$) mixtures remain amorphous liquids, while $LiNO_3$ powder crystallizes rapidly from more concentrated ($n = 0.3$ and 0.2) mixtures. The $n = 0.6$ concentration corresponds to an ether oxygen/Li ratio of 3/1, suggesting that stable amorphous aggregate solvates form, in this case, in which three ether oxygens and one or more anions coordinate the Li^+ cations. When fewer than three ether oxygens are available ($n < 0.6$), phase separation occurs as $LiNO_3$ salt crystals nucleate and grow, leaving more ether oxygens (approximately three) available to coordinate the remaining Li^+ cations as stable amorphous solvates. The crystal structure of anhydrous $LiNO_3$ has been previously determined from a partial single crystal prepared from a melt.[5]

$LiNO_3$ single crystals were also found to form in triglyme $(G3)_n-LiNO_3$ mixtures.[4] A crystalline $(G3)_1$:$LiNO_3$ solvate ($T_m = 31$ °C) forms in $n \geq 1$ mixtures. More concentrated mixtures ($n = 0.8-0.6$), however, remain amorphous liquids on standing at room temperature for several months. Single crystals of $LiNO_3$ separated over several weeks from a liquid $n = 0.5$ mixture.

Large, high-quality block single crystals of anhydrous $LiClO_4$ were prepared from concentrated $(G1)_n-LiClO_4$ mixtures ($n = 0.7$ and 0.5). Other salts such as $LiCF_3SO_3$ and $LiBF_4$ have been shown to form an aggregate $(G1)_{1/2}$:LiX crystalline phase.[6] In contrast, concentrated $(G1)_n-LiClO_4$ mixtures appear to preferentially form an amorphous liquid $(G1)_1$:$LiClO_4$ phase (at room temperature) which may be similar to the crystalline aggregate $(G1)_1$:$LiNO_3$ phase.[7] Phase separation occurs over several weeks in the liquid $n = 0.5$ mixture, resulting in the slow growth of $LiClO_4$ single crystals.[8] ***CAUTION:*** *Note that perchlorate salts of metal complexes with organic ligands are potentially explosive*!

The crystal structure of a lithium perchlorate hydrate, $LiClO_4 \cdot 3H_2O$, is known,[9] and a partial solution for the structure of anhydrous $LiClO_4$ has been previously reported from single crystals prepared from a melt.[10] The $LiClO_4$ structure has more recently also been determined from powder diffraction.[11] Figure 2 shows the packing diagram and local coordination of the Li^+ cations and ClO_4^- anions in the anhydrous $LiClO_4$ single-crystal structure from a crystal prepared using the concentrated glyme technique.[12] The asymmetric unit consists of one lithium, one chlorine, and three oxygen atoms. The orthorhombic unit cell has a space group of *Pnma*, which is related to the space group *Pcmn* previously reported for $LiClO_4$[10] by an axial transformation. Each Li^+ cation has distorted octahedral coordination ($\angle O-Li-O = 76.46(5)-103.54(5)$ and 180°) by six different ClO_4^- anions with O−Li distances of 1.9930(11)−2.3912(11) Å (Table 1). The anions are tetrahedral ($\angle$O−

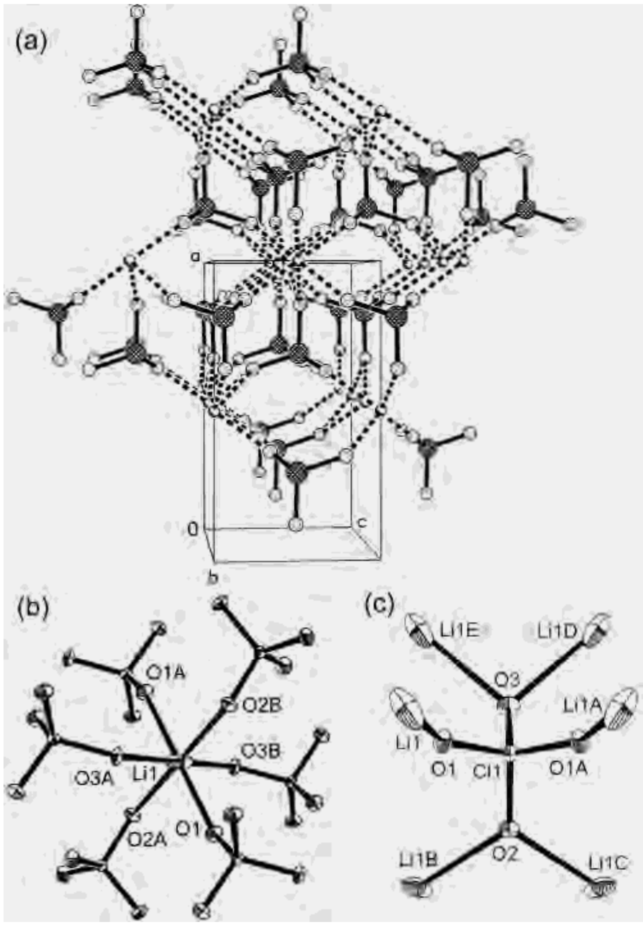

Figure 2. (a) Packing diagram of the anhydrous $LiClO_4$ unit cell (Li shaded, Cl crosshatched, O dotted), (b) Li^+ cation, and (c) ClO_4^- anion coordination. Thermal ellipsoids drawn at 50% probability.

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(4) $LiNO_3$ (Aldrich) was dried by heating under high vacuum at 120 °C for 24 h. G3 and G4 (Aldrich) were dried over 4 Å molecular sieves. $(G3)_n-LiNO_3$ and $(G4)_n-LiNO_3$ mixtures with $n \geq 1$ were prepared by heating the glyme−$LiNO_3$ mixtures while stirring. For more concentrated mixtures, $LiNO_3$ was first dissolved in anhydrous CH_3OH. The G3 or G4 was then added, and the CH_3OH was removed by heating at 60 °C under high vacuum for 12 h. All preparation and storage procedures occurred in a dry room (<1% relative humidity, 22 °C).

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(8) $LiClO_4$ (Aldrich) was dried by heating under high vacuum at 110 °C for 24 h. Anhydrous G1 (Aldrich) was used as received. $(G1)_n-LiClO_4$ mixtures with $n = 1$, 0.7, and 0.5 were prepared by heating the glyme−$LiClO_4$ mixtures while stirring. All preparation and storage procedures occurred in a dry room (<1% relative humidity, 22 °C).

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(12) Crystal data for $LiClO_4$: fw = 106.39, $ClLiO_4$, colorless, blocks (0.44 × 0.32 × 0.32 mm), orthorhombic, space group *Pnma*, $a = 8.6447(12)$ Å, $b = 6.8512(10)$ Å, $c = 4.8254(7)$ Å, $V = 285.79(7)$ Å^3, $D_{calc} = 2.473$ mg m^{-3}, $Z = 4$, $2\theta_{max} = 27.46°$, $\mu = 0.1134$ cm^{-1}, Mo Kα radiation ($\lambda = 0.71073$ Å), $T = -100(2)$ °C. X-ray data were collected using a Bruker SMART CCD area detector diffractometer. The intensity data were corrected for absorption and decay using SADABS (Blessing, R. *Acta Crystallogr. A* **1995**, *51*, 33). The structure was solved via direct methods using SHELXS-97 (*SHELXTL-Plus*, V5.10; Bruker AXS, Inc.: Madison, WI, 1998). Full-matrix least-squares refinement using SHELXL-97 converged with R_1 [$I > 2\sigma(I)$] = 0.0266, wR_2 [$I > 2\sigma(I)$] = 0.0723, R_1 [all data] = 0.0272, wR_2 [all data] = 0.0726 (where $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$ and $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$) for 2239 reflections collected and 352 independent reflections with $I > 2\sigma(I)$ and 35 parameters and 0 restraints.

Table 1. Bond Lengths (Å) and Angles (deg) for $LiClO_4$

Cl1−O1	1.4356(11)	Li1−O1	1.9930(11)
Cl1−O2	1.4531(17)	Li1−O2A	2.1547(11)
Cl1−O3	1.4434(16)	Li1−O3A	2.3912(11)
O1−Cl1−O1A	111.49(10)	O1−Li1−O2A	87.57(5)
O1−Cl1−O2	108.33(6)	O1−Li1−O3A	87.23(5)
O1−Cl1−O3	109.44(6)	O2A−Li1−O2B	180.0
O2−Cl1−O3	109.77(9)	O2A−Li1−O3A	76.46(5)
O1−Li1−O1A	180.0	O3A−Li1−O3B	180.0

Cl−O = 108.33(6)−111.49(10)°) (Table 1). The anions coordinate six different Li^+ cations with two oxygen donor atoms each coordinating a single cation and the remaining two coordinating two cations each. The Cl−O distances are 1.4356(11)−1.4531(17) Å (Table 1). The thermal ellipsoids of the atoms (Figure 2) indicate that the ClO_4^- anions are rigidly fixed in position, but the Li^+ cations rattle somewhat within the cage created by the anion oxygens. This single-crystal structure agrees well with the powder diffraction structure, but a higher precision is found for the single-crystal structural solution.

The multidentate donor nature and flexibility of glyme solvents enable a wide range of solvates to form with electron acceptors (e.g., cations) incorporating one or more glyme molecules in the solvate structures. This diversity of solvate structures may be the origin of the slow phase separation of the salts enabling high quality solute single crystal growth. The concentrated glyme−salt crystallization technique is therefore a relatively simple general procedure for the preparation of large, high-quality single crystals of a number of anhydrous salts and other materials which are solvated by glymes.

Acknowledgment. W.A.H. is indebted to the National Science Foundation and the University of Minnesota for the award of Graduate Research Fellowships.

Supporting Information Available: Crystallographic data file for $LiClO_4$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC034518Q